SPECTRAL CHARACTERIZATION OF CARBOXYLIC ACIDS, AMINO ACIDS AND AMMONIUM SALT AS THE CARRIERS OF 3.2 µm BAND OF COMET 67P/CHURYUMOV-GERASIMENKO

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Introduction: The VIRTIS instrument (Visible InfraRed Thermal Imaging Spectrometer) aboard of the Rosetta spacecraft has collected hyperspectral images of the surface of comet 67P in the 0.4-5 µm range. It revealed a broad feature centered at 3.2 µm in the reflectance spectra of comet 67P/CG, which might be consistent with the presence of semi-volatile organics, also possibly detected by the COSAC and PTOLEMY instruments [1-4]. Carboxylic acids have been proposed as candidates as these molecules in the liquid form display a broad absorption band that fit that of the 3.2 µm band and carboxylic acids are also the main component in the soluble organic fraction in primitive meteorites, with several tens of carboxylic, dicarboxylic and hydroxylated acids identified so far [5]. In this study, we have focused on the experimental spectral characterization of the carriers of the band at ~ 3.2 µm with particular attention to amino acid and carboxylic acids whose spectral properties in the solid state are poorly known, as well as to the ammonium ion.

Methods: Experiments were run at IPAG with a Vertex 70v FTIR spectrometer equipped with a GLOBAR-source and a DTGS detector for transmittance spectra. Thin films of low weight carboxylic acids were condensed as ices on a KBr window held at 25 K, and warmed up with a resistor and a PID controller (Lake Shore 331) until the sublimation of the acid. Carboxylic acids which are available in the solid state at room temperature were prepared with a spin coater, by deposition in a vacuum furnace and as pellets. Mid-infrared spectra (4000 – 400 cm^{-1}) were collected with a 4 cm^{-1} spectral resolution. The reflectance spectra of mixture of carboxylic acid with graphite, basalt and olivine (as analogs of dark refractory cometary materials) were collected using a home-made spectro-gonio radiometer and an environmental cell (10^{-5} mbar, -15ºC - 60ºC) in the spectral range 500-4200 nm.

Results and Discussion: The transmittance IR spectra show that C1-C4 carboxylic acids with an aliphatic side chain display a broad feature in the 3 µm region that is controlled by the -OH group, onto which are superimposed C-H stretching modes [6]. This band has however components towards long wavelengths (3.6-4.1 µm), which do not appear in comet spectra. Above C5, the prominent and sharp aliphatic massif at 3.4 µm dominates the 3 µm region and does not account for the broadness of the 3.2 µm feature. For dicarboxylic (C4 fumaric acid) and hydroxylated acids (C2 glycolic and C3 lactic acids), the presence of several –OH groups leads to a broadening of the 3 µm feature with respect to their related monocarboxylic acids, however side bands between 3.6 and 4.2 µm are still present. We also investigated carboxylic acids containing aromatic species in their side chain that display intense and complex features around 2.9-4.0 µm and they do not appear as good candidates for accounting the 3.2 µm band in comet spectra. For Amino acids that contain –OH and NH_3 bonding produce a broader feature (3-4.2 µm) due to the formation of Zwitter-ions Ammonium salts show the strong absorbance in 2.8-3.7 µm range due to antisymmetric and symmetric NH stretchings and gradual decrease in intensity is often observed toward the lower-frequency[6].

Reflectance spectra of sub-micrometric graphite grains mixed with acids or ammonium ions display a very low reflectance and none features appears in the 3 µm region [7]. Using more transparent matrices as basalt and olivine made it possible to observe features in the 3 µm range. We observed that mixtures of acids/salt with olivine generate a drop continuum that starts from 2.7 µm. Several spectra of carboxylic and amino acids have a very broad reflectance band which do not ecompass the 3.2 µm in the spectrum of 67P. The grain size appeared as a key parameter that controls the shape and width of the band, in particular the absorption continuum towards large wavelength. We will emphasize experimental protocols that allow to accurately control grains size.

Conclusion: Simple carboxylic acids have a broad band (2.8-4.2 µm) that does not fit the comet spectrum. Larger acids are not good candidates neither. Ammonium ions might contribute to the 3.2 µm band. Overall, the lack of features for mixtures with a dark refractory material (graphite) raises the question of the nature of the mixture at the surface of the comet: intimate or areal. Developments of experimental protocols producing sub-micromteric material appeared as the angular stone of reflectance measurements.

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